

BULK VISCOSITY OF LIQUID ARGON, KRYPTON AND XENON

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The bulk viscosities of liquid argon, krypton and xenon along their liquid-vapor coexistence curves have been deduced from Brillouin linewidth measurements. Our results agree with ultrasonics data, where available, and with both corresponding states law predictions and molecular dynamics simulation.

Experimental values of transport coefficients of rare gas liquids are a valuable aid in testing statistical mechanical theories and molecular dynamics simulations of the liquid state. When the thermal conductivity and the shear viscosity of a liquid are known, the bulk viscosity can be deduced from Brillouin scattering linewidth measurements. Using this method we have determined values of the bulk viscosity along the liquid-vapor coexistence curve: for xenon from the triple point to fifteen degrees below the critical point; and for argon and krypton near their respective triple points. In a preliminary report of our results of the temperature variation of $(\alpha/f^2)_{\text{exp}}$ for xenon [1] the values of η_β derived from the linewidth data are incorrectly stated. Corrected values are given here.

The polarized Rayleigh-Brillouin spectrum is caused by density fluctuations [3]. The theoretical intensity distribution can be deduced from the usual linearized hydrodynamic equations [4] and consists of a triplet: 1) a central lorentzian called the Rayleigh line and 2) a pair of satellite Brillouin lines shifted from the center frequency by f (H_2)

$$f = \pm qv/2\pi \quad (1)$$

where v is the sound velocity [1, 2] and q the wave vector

$$q = \frac{4\pi n \sin(\theta/2)}{\lambda_0} \quad (2)$$

n being the refractive index of the sample [5], λ_0 the vacuum wavelength of the incident light (514.5 nm) and θ the scattering angle.

The Brillouin lines are broadened by sound absorption and their full widths at half maximum are (in H_2):

$$\Gamma = \frac{q^2}{2\pi\rho} \left[\frac{(\gamma-1)}{C_p} K + \frac{4}{3}\eta_s + \eta_\beta \right] \quad (3)$$

where ρ is the density [6], γ the specific heat ratio [7], C_p the specific heat at constant pressure [7], K the thermal conductivity [8], η_s the shear viscosity [9] and η_β the bulk viscosity.

The Brillouin lines are composed of the sum of a lorentzian and a dispersion curve (anti-symmetric lorentzian). In the present case where $\Gamma \ll f$ the contribution of the dispersion curve is negligible.

Therefore measuring Γ accurately one deduces the bulk viscosity. Our measurements were performed using a high resolution (~ 18 MHz) confocal Fabry-Perot interferometer. Backscattering geometry was employed to maximize the linewidths and minimize the error in determining q (which is nearly independent of angle for large angles). The aperture was quite small (subtending an angle of ~ 5 milliradians) so that with backscattering geometry the aperture broadening was of the order of 1%.

The sample was contained in a pressure cell suspended from a liquid nitrogen dewar. The temperature was controlled to $\pm 0.01^\circ\text{K}$. Measurements of Brillouin velocities [2] agreed with ultrasonics values to better than 0.2% indicating that the experimental parameters were determined accurately.

The instrumental function was deconvoluted from experimental data by the method of Leidecker and

Table 1

Summary of the values of $(\alpha/f^2)_{\text{exp}}$, Γ and V deduced from the light scattering experiments. The values of $(\alpha/f^2)_{\text{cl}}$ and η_s were calculated using the data of [9] and η_β was calculated from eq. (4).

	$T(\text{K})$ ± 0.02	$f(\text{GHz})$ ± 0.010	$\Gamma(\text{MHz})$ ± 5	V (ms^{-1}) ± 2.0	Experimental $\alpha/f^2 \times 10^{16}$ $(\text{cm}^{-1} \text{s}^2) \pm 10\%$	Classical $(\alpha/f^2) \times 10^{16}$ $(\text{cm}^{-1} \text{s}^2) \pm 10\%$	$\eta_s \times 10^3$ $(\text{gm cm}^{-1} \text{s}^{-1})$ $\pm 5\%$	$\eta_\beta \times 10^3$ $(\text{gm cm}^{-1} \text{s}^{-1})$ $\pm 12\%$	η_β/η_s $\pm 15\%$
Argon	85.68	4.050	61	848	1.42	1.14	2.67	1.20	0.43
	89.32	3.915	63	823	1.56	1.16	2.38	1.48	0.62
	97.92	3.597	56	762	1.77	1.27	1.82	1.80	0.99
	99.08	3.553	59	753	1.93	1.28	1.75	1.85	1.06
	107.78	3.212	57	687	2.51	1.47	1.38	2.23	1.62
	109.60	3.138	58	627	2.69	1.53	1.31	2.30	1.76
Krypton	117.12	3.501	62	693	2.32	1.84	4.32	2.05	0.47
	120.44	3.423	63	680	2.49	1.85	4.00	2.28	0.57
	121.71	3.400	62	676	2.48	1.87	3.90	2.37	0.61
	125.26	3.307	62	659	2.70	1.93	3.65	2.62	0.72
	126.71	3.276	63	651	2.78	1.95	3.56	2.71	0.76
	131.13	3.214	63	643	2.99	2.15	3.30	3.00	0.91
Xenon	168.63	3.396	63	633	2.7	2.27	4.77	1.7	0.35
	182.83	3.145	58	594	3.1	2.41	3.75	2.0	0.53
	206.81	2.712	48	523	3.9	2.80	2.71	2.1	0.78
	210.65	2.639	43	510	3.8	2.93	2.57	1.6	0.62
	229.12	2.292	43	450	5.8	4.27	2.04	1.7	0.83
	253.45	1.765	49	356	14	8.65	1.54	2.7	1.77
	270.54	1.333	52	276	34	17.02	1.21	3.5	2.90

La Macchia [10] and also by numerically convoluting the instrument function with test lorentzians [11, 12]. The methods agreed to better than 3 MHz.

The data from the light scattering experiments in argon, krypton and xenon is summarized in table 1 together with the values of $(\alpha/f^2)_{\text{cl}}$ and η_s calculated using the data from ref. [9]. Values of the bulk viscosity

$$\eta_\beta = [(\alpha/f^2)_{\text{exp}} - (\alpha/f^2)_{\text{cl}}] 2\rho_0 V^2/4\pi \quad (4)$$

where $(\alpha/f^2)_{\text{exp}} = \pi\Gamma/Vf^2$ are also given in the table. The data for argon agree [2] within experimental error with the ultrasonics values reported by Naugle [15] and by Cowan and Ball [16]. We note that for all three of the rare gas liquids the ratio η_β/η_s at the triple point is ~ 0.4 .

The values of η_β for xenon near the triple point predicted using the law of corresponding states with our values for argon and krypton and the data of Larson et al. [13] for neon are in the region $2.1 \sim 2.2 \times 10^{-3}$ poise. Molecular dynamic simulations of

Levesque et al. [14] predict a value of $\sim 1.7 \times 10^{-3}$ poise.

In conclusion, we find our measurements of the bulk viscosity of the rare gas liquids to be internally consistent by corresponding states arguments and in agreement with the results of ultrasonics and molecular dynamics simulation. However, we do not agree with the findings of Rand and Stoicheff [17] who deduce a value of zero for the bulk viscosity of argon from their measurement of Γ . The value reported here for argon at 85 K is 61 ± 5 MHz and that of [17] (when converted to the same q value) is 47 ± 5 MHz. In [17] Γ was obtained from the experimental data by a deconvolution process which used the Rayleigh line $(kq^2/\rho C_p)$ as equivalent to the instrument function. However, this procedure is not valid in this case since the linewidths were of comparable magnitude ~ 15 MHz. Consequently the calculated value of Γ and η_β in [17] will be less than the actual values.

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